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Assessing pollution in the Kola River, northwestern Russia, using metal concentrations in water and bryophytes

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Intensive Cu-Ni and Fe mining and smelting in northwestern Russia constitutes a potential risk of pollution in the Kola River. We assessed the degree of pollution along the Kola River by means of overall water quality evaluation and analyses of metals in water samples (dissolved and particulate fractions) and aquatic mosses. The observed pollutant levels were compared with those in unpolluted reference rivers. The results indicate relatively low overall contamination in the Kola River, although Cu and Ni levels are elevated relative to the reference data. Furthermore, PCA ordination models identified clear metal concentration patterns along the river. Al, Cd, Co, Fe, Pb and Zn exhibited an almost continuous increase from the headwaters to the river mouth, whereas As, Ba, Cu, Mn, Mo and Ni showed their highest concentrations in the headwaters, close to the mining areas, relatively low concentrations in the middle parts of the river and elevated concentrations at the river mouth. Bryophyte analysis appeared to be a more sensitive tool for metal pollution assessment than metal concentrations in water.

Introduction

The Kola River in the northern part of the Kola Peninsula is economically important for northwestern Russia. The river is vital for the reproduction of salmon in this region and an important source of drinking water for 500 000 people of the city of Murmansk and the surrounding settlements. Industrial development, especially the large iron ore mine and concentration plant at Olenegorsk and the Cu-Ni smelter at Monchegorsk, has increased the risk of metal pollution in the river. No comprehensive assessment of the pollution status of this important river basin has been made, however.

Metal concentrations in river ecosystems are mainly affected by the geology of the drainage area, the weathering tendency of the bedrock and anthropogenic factors (Berner and Berner 1996). As the toxicity and environmental fate of metals

are dependent on their speciation in streams, information on both dissolved metal concentrations and the amounts associated with particulates is important for the assessment of pollution status (Moore and Ramamoorthy 1984). Trace metal concentrations in water are often close to the analytical detection limits of the instruments, however, and peak concentration periods may be of very short duration (Philips and Rainbow 1993, Claveri *et al*. 1995). Furthermore, metal concentrations can fluctuate drastically, depending on dilution effects due to variations in water discharge (Philips and Rainbow 1993). The reliability of a pollution status assessment can be increased by evaluating both metal concentrations in water and metal concentrations in bioindicators, such as certain aquatic bryophytes.

Aquatic bryophytes (e.g. *Fontinalis* spp.) are considered ideal indicators of metal pollution in a wide range of river types (Say and Whitton 1983, Vanderpoorten 1999, Vuori *et al*. 2003). They are widely distributed, long-lived, have a considerable capacity to accumulate heavy metals and are relatively tolerant of metal pollution (Lopez and Carballeira 1993). Since bryophytes do not possess roots or vascular systems, there is no internal transfer of pollutants (Cenci 2000, Nimis *et al*. 2002). Metal uptake in bryophytes occurs primarily straight from the water, by adsorption and absorption through the cell surfaces (Welsh and Danny 1980, Empain 1985, Cenci 2000). Bryophytes accumulate ambient metal concentrations and retain the increased levels for several days or even weeks after concentrations in the water have decreased. This enables the monitoring of both chronic metal contamination and sudden discharges (Say and Whitton 1983, Wehr and Whitton 1983, Mouvet *et al*. 1993).

The aim here was to assess the pollution status of the Kola River using data on dissolved (< 0.22 μm) and particulate (> 0.22 μm) metal concentrations in the river water and metal residues in aquatic mosses. We also assessed the relationship between metal accumulation in mosses and metal concentrations in the dissolved and particulate fractions in the river and compared the metal levels in the river water and bryophytes of this arctic–boreal river basin with uncontaminated reference sites in northern Europe, namely the Kalix River in northern Sweden (Pontér *et al*. 1992, Ingri 1996, Ingri *et al*. 1997, 2000, 2005), some non-polluted streams draining woodlands in northern Sweden (Alm *et al*. 1999) and the Tenojoki (Hämäläinen *et al*. 1996) and the Näätämöjoki in northern Finland and Norway.

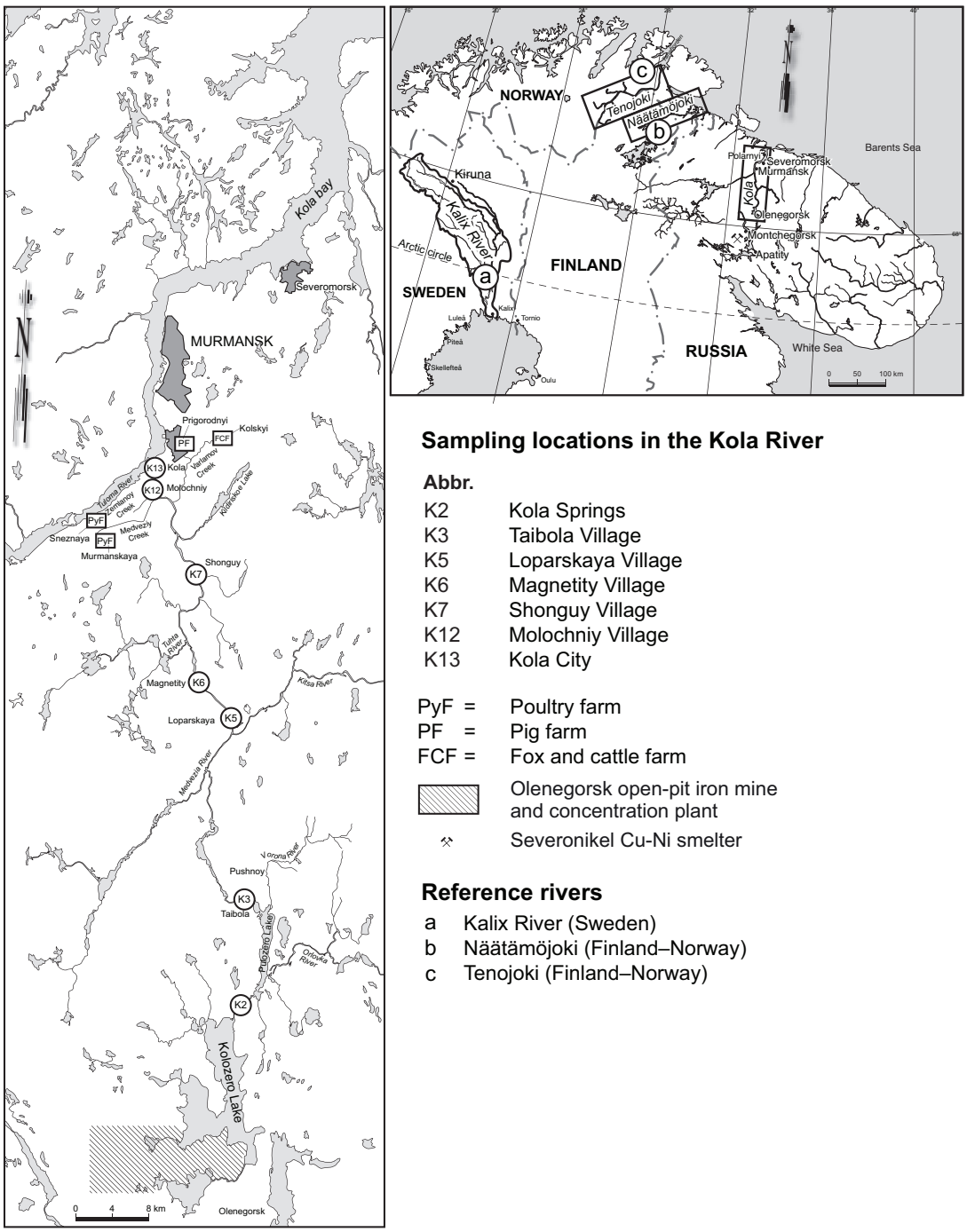
Methods

Area descriptions

The Kola River

The drainage area of the Kola River is located towards the north of the central part of the Murmansk region (69°N, 33°E) and covers 3850 km^2. The river originates in Kolozero, close to the city of Olenegorsk, and it flows 83 kilometres directly northwards, passing through the lakes Pulozero and Murdozero on the way to the Kola Bay in the Barents Sea (Fig. 1). The annual mean water discharge of the Kola River is about 30 m^3 s^{-1} (Murmansk Areal Department for Hydrometeorology and Environmental Monitoring unpubl. data). The basin is located mainly in the northern boreal coniferous zone (Reimann *et al*. 1998), and 54% of its area is forested (Jonsson and Mikaelsson 1997). Lakes within the basin have a total surface area of 218 km^2, which is 6% of the basin area. About 15% of the basin is covered by wetlands (Mokrotovarova 2000). The rocks within the basin are felsic gneisses, granites, tonalities, iron quartzite and amphibolites, and the main Quaternary deposits are till and peat (Reimann *et al*. 1998).

The main polluters within the Kola River basin (Fig. 1) are the Olenegorsk open-cast iron ore mine and concentration plant in the upper part and agricultural enterprises such as poultry, pig, fox and cattle farms in the lower part (Jonsson and Mikaelsson 1997, Mokrotovarova 1999, Rytter 2001). The Severonikel Cu-Ni smelter at Monchegorsk is located 25 km south of the catchment area (Fig. 1), but is a major source of airborne pollution within it, especially during the wintertime, when the dominant wind direction within the basin is from the south and southwest (Mokrotovarova 1999). The open-pit iron mine



Sampling locations in the Kola River

Abbr.

K2	Kola Springs
K3	Taibola Village
K5	Loparskaya Village
K6	Magnetity Village
K7	Shonguy Village
K12	Molochniy Village
K13	Kola City

PyF = Poultry farm
PF = Pig farm
FCF = Fox and cattle farm

Olenegorsk open-pit iron mine and concentration plant

⚒ Severonikel Cu-Ni smelter

Reference rivers

a Kalix River (Sweden)
b Näätämöjoki (Finland–Norway)
c Tenojoki (Finland–Norway)

Fig. 1. The Kola River basin and the locations of the sampling stations and main pollution sources. The reference river basins are shown in the right-hand side map.

and ore concentration plant in Olenegorsk are located between two lakes, Imandra and Kolozero. Besides a leakage of sludge deposits, there was a discharge of improperly treated mine and process waters from the steelworks directly into Kolozero that constituted 0.4×10^6 m^3 in 2002

(Federal State Institution Murmansk Territorial Fund for Geological Information 2003). The pollutants from the Olenegorsk open-cast iron ore mine and concentration plant reach the Kola River via Kolozero, while leakage from the overloaded manure ponds at the poultry farms (Rytter 2001) reaches it via the Medveziy and Zemlanoy creeks and pollutants from the pig, fox and cattle farms via the Varlamov creek (Fig. 1).

Reference rivers

The drainage basin of the Kalix River (Fig. 1), covers an area of 23 600 km^2 in the boreal zone in northern Sweden (66°N, 23°E), is one of the last major pristine rivers in Scandinavia and in Europe (Dynesius and Nilsson 1994). The catchment area is covered mainly by coniferous forests (55%–65%) and peatlands (16%–20%). Lakes cover 4% of the area, and less than 1% is farmland (Hjort 1971). The dominant rock types are granites of age 2.1–1.8 Ga, mica schists, quartzite and amphibolites (Gaal and Gorbatschev 1987). The annual mean water discharge is about 300 m^3 s^{-1}. A data set was constructed from measurements made near the river mouth on 90 occasions between April 1990 and October 1992 (Ingri 1996).

The Näätämöjoki (Fig. 1) is a river located in northern Scandinavia (69°N, 28°E). Its basin area is 2962 km^2, with 79.5% lying on the Finnish side of the border and the rest on the Norwegian side. The river originates in Iijärvi and flows 79 km northeast to the Neiden Fjord in the Barents Sea. The river basin forms a part of the oldest bedrock area in northern Lapland and is dominated by acidic granite-gneisses (Manner and Tervo 1988, Ekholm 1993). There is no industry, mining, peat mining, agriculture or animal husbandry in the basin, the main forms of land use being reindeer herding, hunting, tourism and hiking (Kojola 1993). According to data on water chemistry and biological parameters, the ecological state of the Näätämöjoki is excellent (Finnish Environment Institute (SYKE) and Regional Environment Centres 2005). We used reference bryophyte (*Fontinalis dalecarlica*) data for a site located about 12 km upstream from the river mouth sampled in July 2002.

The Tenojoki flows along the border between northern Norway and Finland (70°N, 28°E) and is one of the largest salmon rivers in Europe (mean discharge 163 m^3 s^{-1}, catchment area 13 386 km^2) (Fig. 1). Its sources are in the treeless arctic mountain areas, from where it flows 382 km northeast and enters the Tana Fjord in the Barents Sea. Lakes occupy only 3.1% of the area of the basin. The main bedrock type within the basin is gneiss, while sandstones and amphibolites predominate in the lower part. Trace metal concentrations in the water, aquatic bryophytes (*Fontinalis antipyretica, Scapania* spp.) and caddis larvae (*Hydropsychidae*) are low (Huru *et al*. 1996, Hämäläinen *et al*. 1996, Traaen 1996). Reference bryophyte data were obtained from the report by Hämäläinen *et al*. (1996).

Water chemistry

Sampling

The dissolved (< 0.22 μm) and particulate (> 0.22 μm) phases were sampled at seven points along the Kola River, K2, K3, K5, K6, K7, K12 and K13 (Fig. 1), on five occasions between July 2001 and July 2002 (8–11 July 2001, 24–27 September 2001, 17–19 April 2002, 15–17 May 2002 and 8–12 July 2002).

Water temperature, conductivity, dissolved oxygen and pH were measured *in situ* using a Hydrolab® Surveyor II water quality probe calibrated before and after each day in the field. Samples of stream water were collected using a TYGON tube, lowered 30 cm below the water surface at a distance of about three metres from the river bank. The acid-cleaned tubing was connected to a portable peristaltic water pump (Masterflex®). The tubing system was rinsed with four to five litres of water before taking the samples.

0.22 μm filters are frequently used to separate dissolved and particulate phases (e.g. Pekka *et al*. 2004, Gelting 2006). The particulate (> 0.22 μm) and dissolved (< 0.22 μm) phases in the samples were separated out by filtering the water in the field (except in April 2002) through two parallel-mounted 0.22-μm Millipore® cellulose mem-

brane filters of 142 mm in diameter mounted in Geotech® polycarbonate filter holders, and collected in acid-washed polyethylene bottles. The filters were rinsed in 5% acetic acid before sampling. Four filters were used for each sample: two to determine major elements and two for trace elements. Water was pumped in until the filters were clogged. The dissolved phase was sampled after one litre of water had passed through the two filters, and the total volume of water filtered was measured for each pair of filters. In April 2002, the water samples were filtered at the laboratory of the Murmansk Area Department for Hydrometeorology and Environmental Monitoring within two to four hours of sampling.

Total organic carbon (TOC) was sampled with a Falcon® plastic tube filled with 12.5 ml of water and 100 μl of 2M HCl. Particulate organic carbon (POC) was collected on Whatman® GF/F filters of 0.7 μm pore size that had been precombusted for one hour at 500 °C and mounted in a stainless steel filter holder. The volume of the filtered water was measured. We also collected unfiltered water samples for analyses of alkalinity and TOC. All the water samples were stored in a refrigerator and all the filter samples with particulate material were stored in a freezer until analysis.

Analytical methods

The samples were analysed in cooperation with Analytica AB in Luleå, Sweden, a laboratory accredited in accordance with the international standards ISO 17025, ISO 9001:2000 and ISO/IEC Guide 25. The analyses of trace and major elements were performed using optical emission spectrometry (ICP-AES) and sector field mass spectrometry (ICP-SFMS) with inductively coupled plasma as the excitation source. The instrumental precision determined as ± 1 SD for three to four runs of the same sample was better than 4% for all the elements reported except for dissolved Cu, particulate Co and particulate Zn, where the precision was ± 9%.

Particulate fraction

Two filters were wet-ashed in 14 M HNO_3 in Pt crucibles and then dry-ashed at 550 °C. The ash was then fused with $LiBO_2$ in graphite crucibles at 1000 °C according the method described in detail by Burman *et al*. (1978) and its application for particulate matter described by Ödman *et al*. (1999), and the resulting bead was dissolved in suprapur conc. HNO_3 and analysed by ICP-AES and ICP-SFMS. The two remaining filters were digested in 8 ml of 14 M suprapur HNO_3 and one ml of 30% H_2O_2 in Teflon bombs heated in a microwave oven. Particulate Co, Cr, Cu, Mn, Mo, Ni, Pb, S and Zn were then analysed using ICP-AES and ICP-SFMS. The particulate organic carbon (POC) analyses were performed with a Carlo Erba® model 1108 high-temperature combustion elemental analyser using standard procedures at the temperature of 1030 °C.

Dissolved fraction and unfiltered water samples

The filtered water was analysed for major and trace elements by ICP-AES (Ca, K, Mg, Na, S and Si) and ICP-SFMS (Fe, Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, P, Pb, Sr and Zn), while Cl^-, NO_3^-, NO_2^- and NH_4^+ were determined by ion chromatography. The TOC analyses were performed with a Shimadzu® TOC-5000 high-temperature combustion instrument. Alkalinity was determined with autotitration according to Gran's method. The same methodology of sampling and analysis as described above was used for the Kalix River, except that the filtration was done with 0.45-μm instead of 0.22-μm pore size filters.

Aquatic bryophytes

Sampling

Aquatic bryophytes (both whole and young terminal shoots) were sampled at seven sites along the Kola River, K2, K3, K5, K6, K7, K12, K13 (Fig. 1), on two occasions (8–11 July 2001 and

8–12 July 2002). The species concerned were *Fontinalis antipyretica* at sites K2, K3, K5, and K7, *Fontinalis dalecarlica* at site K6 and *Hygrohypnum ochraceum* at sites K12 and K13, since no *Fontinalis* species were found there.

One to two litres of mosses (three to five tufts) were collected from each site using plastic gloves, rinsed in river water to remove sand and other particles and gently squeezed before being placed in clean plastic bags. The sampling was restricted to submerged plants growing in a relatively constant current and as far as possible in the middle part of the stream bed. The samples were frozen within two to six hours of collection.

Analytical methods

The moss samples were pre-treated in the environmental laboratory of the West Finland Regional Environment Centre in Kokkola, Finland (Finnish Accreditation Service, EN ISO/IEC 17025). The terminal light green tips (representing annual growth) (Johnson 1976) were separated from the whole shoots and all parts were washed with distilled water. Five replicates were made from each sample. All the laboratory equipment was washed in acid. The samples were freeze-dried at –40 °C and their dry weight determined. They were then digested with 3.0 ml of HNO_3 and heated at 60 °C for two hours and subsequently at 110 °C for six hours. The digest was made up to a final volume of 20 ml with distilled water (Finnish Standards Association, SFS 5075). Analyses of metal concentrations (Al, As, Ba, Cu, Cd, Co, Fe, Mn, Mo, Pb, Zn and Ni) were carried out using the ICP-MS technique (in-house methods K206 and K208) at the laboratory of the Finnish Environment Institute in Helsinki, Finland (Finnish Accreditation Service, EN ISO/IEC 17025). In the case of the 2001 samples and all the *Hygrohypnum ochraceum* samples only whole shoots were analysed.

Data analysis

With the sign test (Zar 1996) we analyzed differences in element concentrations in the whole shoots of the bryophytes between 2001 and 2002 and between whole and young terminal shoots of *Fontinalis* spp. samples in 2002. Principal component analyses (Sharma 1996) were performed to reduce the 12 metal element variables (Al, As, Ba, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, Zn) to a few essential components, so that the uncorrelated principal components (PCs) extracted from these analyses would represent linear combinations of originally correlated variables. Only principal components that explained > 10% of the variance among metal concentrations were considered. Component loadings $|> 0.7|$ were used to interpret the PCs. Separate PC analyses were performed on the metal concentrations in (a) the dissolved fraction, (b) the particulate fraction and (c) the whole moss shoots. The scores (± SD) on the principal components for each sampling station (K2, K3, K5, K6, K7, K12 and K13) were used to discriminate among the stations. The differences in bryophyte metal concentrations between the Kola River and the reference sites and the differences in enrichment ratios between the elements were analysed with a Mann-Whitney *U*-test (Zar 1996).

Results

Water quality

Total dissolved solids (TDS) in the water of the Kola River were on average low, 35 mg l^{-1} (Ca (3.3 mg l^{-1}) + Na (2.8 mg l^{-1}) + Mg (1.4 mg l^{-1}) + K (0.8 mg l^{-1}) + HCO_3 (14.3 mg l^{-1}) + SO_4 (5.4 mg l^{-1}) + Cl (2.7 mg l^{-1}) + SiO_2 (3.8 mg l^{-1})) compared with those in "average river water" (100 mg l^{-1}, Berner and Berner 1996) and were similar to those in the Kalix River, where the average TDS is 33 mg l^{-1} (Ingri 1996). The mean conductivity (EC) was 75 μS cm^{-1} (Fig. 2a) in the headwaters downstream of the mining area (K2), i.e. nearly twice that in the middle part of the river (sites K5–K7). The EC then remained at a constant level of around 40 μS cm^{-1} through the middle reaches, increasing slightly in the lower part of the basin (sites K12 and K13). Average oxygen saturation varied from 80% to 90% (Fig. 2a), and the water was close to neutral, with an average pH of about 7.0 (Fig. 2b), except for

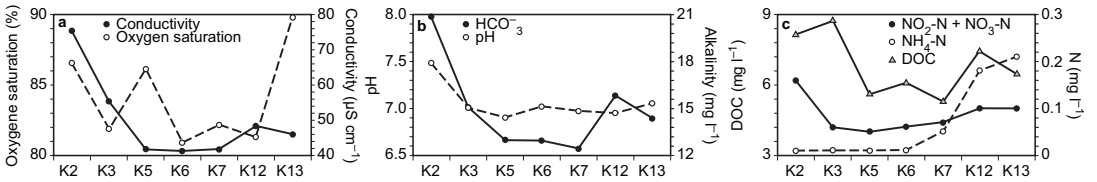


Fig. 2. Distributions of (**a**) average O_2 saturation and conductivity, (**b**) pH and alkalinity, and (**c**) DOC and NH_4-N, NO_2-N + NO_3-N in the Kola River (n = 5 for each sampling site, July 2001–July 2002).

the headwaters (K2), where the pH was ≥ 7.5. Average alkalinity varied from 12.4 mg l^{-1} to 21 mg l^{-1}, with elevated values downstream of the mining areas (sites K2–K3) and of the agricultural areas (sites K12 and K13) (Fig. 2b).

The Kola River had low concentrations of nitrogen (Fig. 2c) and phosphorus: < 0.1 mg l^{-1} for NO_2-N + NO_3-N, 0.01 mg l^{-1} (K2–K7) and 0.2 mg l^{-1} (K12–K13) for NH_4-N, and < 5 μg l^{-1} (K2–K7) and ≈ 10 μg l^{-1} (K12–K13) for dissolved P. Approximately 97% of TOC passed through the 0.7-μm filter (referred to as dissolved organic carbon, DOC). The average DOC in the river was 5–9 mg l^{-1}.

The concentrations of dissolved As, Cu, Mo and Ni and particulate Mn at the outflow from Kolozero (K2) downstream of the mining areas were two to five times higher than those in the middle part of the river (sites K5–K7) (Table 1 and Fig. 3). The concentrations of dissolved Al, Fe and Zn and particulate Al, Fe and Co showed an almost continuous increase from the headwaters (K2) to the river mouth (K13) (Fig. 3). Increases in the concentrations of dissolved Co, Mn and As and particulate Zn, Pb and Ba were measured at K12 (Fig. 3).

The 12 metal variables in the dissolved and particulate fractions were reduced to two PCs (Fig. 4). The PCA based on metal measurements in the dissolved fraction explained 60.1% of their variance in the dissolved fraction (PC1 31.9% and PC2 28.2%) and 57.9% in the particulate fraction (PC1 34.5% and PC2 23.4%). In the dissolved fraction PC1 represented a gradient of increased concentrations of Ni, Mo and Cu and decreased concentrations of Ba and Fe, while PC2 represented a gradient of increased concentrations of Al, Mn, Zn and Co (Fig. 4a). Fe, Ba, As, Cd and Pb did not contribute significantly to the formation of the two PCs (Fig. 4a) and were thus of minor importance for discriminating between the sampling stations. In the particulate fraction, PC1 represented a gradient of increased concentrations of Co, Pb, Fe and Al, whereas PC2 represented increased concentrations of As, Mo and Ni, with Mn, Cd, Ba, Cu and Zn showing no significance (Fig. 4b).

Stations K2 and K3 could be distinguished from each other and from the remaining stations in terms of PC1 for the dissolved fraction (Fig. 4a), K2 having higher metal concentrations along the Ni, Mo and Cu gradient than K3, for example, but they could not be discriminated from each other on the Al, Mn, Zn and Co gradient (PC2). Stations K2 and K3 could also be separated clearly from K7, K12 and K13 on PC1 for the particulate fractions (Fig. 4b), as they reflected generally lower particulate metal concentrations on the Co, Pb, Fe and Al gradient. In addition, K7 could be discriminated from K2 and K3 on PC1, K6 from K2 and K12 from K13, while K12 and K13 could be discriminated from K2, K3 and K6. The particulate phase also indicated a difference between K2 and K6 on PC2, i.e. the As, Mo and Ni gradient (Fig. 4b).

Aquatic bryophytes

The metal concentrations in the whole shoots of *Fontinalis* spp. from the Kola River (sites K2–K7) were in general higher than those in the young terminal shoots. This difference was statistically significant (sign test: $p < 0.05$) for Al, As, Ba, Co, Fe, Mn, Mo and Zn. On the other hand, there were no significant differences in the metal concentrations in the whole moss shoots between the years 2001 and 2002 (sign test: $p < 0.05$).

The concentrations of Al, Cd, Co, Fe, Pb and Zn in bryophytes (whole shoots) showed a clear

increase downstream, with their highest values at K13 (Fig. 3), while the levels of As, Ba, Cu, Mn, Mo and Ni decreased notably from K2 to K3, were fairly constant throughout the middle reaches (K5–K7), but increased again in the lower course (K12–K13).

The PCA for metal concentrations in the whole moss shoots differed significantly among the sampling sites (Fig. 4c) and explained 87.9% of the variance (PC1 55.4% and PC2 32.5%), as compared with < 61% for the metal concentrations in the water. PC1 represented a gradient of increased concentrations of As, Ba, Cu, Mn, Mo and Ni and PC2 of Al, Co, Fe, Pb and Zn (Fig. 4c). All the elements in the moss PCA model except for Cd contributed significantly to the formation of the PCs. This PCA model discriminated among sampling sites in terms of both PC1 and PC2. K2 showed higher metal concentrations than K5–K7 or K12 on the As, Ba, Cu, Mn, Mo and Ni gradient (PC1), where K6 could also be distinguished from K13. K2 could be discriminated from all the stations except for K3 on PC2, i.e. the Al, Co, Fe, Pb and Zn gradient (Fig. 4c), showing the lowest concentrations of these elements. K3–K7 could also be distinguished from K12 and K13 on PC2. To summarize the results of the moss PCA model, we grouped the sampling stations into three clusters, i.e., the first represented by K2, the second by K3–K7 and the third by K12 and K13.

The sequence of enrichment ratios, i.e. the concentration of a given metal in the whole moss shoots divided by the total metal concentration in the water, was Mn > Co > Zn > Cd > Fe = Al = Pb = Ni = Ba > Cu > As > Mo (Mann-Whitney

Table 1. Average[a] dissolved[b] and particulate[c] metal concentrations (μg l^{-1}) in the water of the Kola River, compared with the average for the Kalix River (Ka) and the average for river water (ARW). Averages calculated with the values below the detection limit (dl) are set to 1/2 dl.

Parameter	K2	K3	K5	K6	K7	K12	K13	Ka[d]	ARW[e]
Diss. Al	6.2	17.1	28.6	27.1	28.7	28.8	36.0	16	40.0
Part. Al	4.0	6.5	10.4	7.1	17.8	24.7	29.5	34	
Diss. As	0.15	0.10	0.08	0.07	0.08	0.11	0.10	0.14	1.0
Part. As	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	
Diss. Ba	3.7	3.5	4.4	4.6	4.8	5.2	4.9	7.2	60.4
Part. Ba	0.32	0.24	0.22	0.18	0.25	0.38	0.37	0.51	
Diss. Cd	0.006	0.004	0.014	0.006	0.006	0.014	0.005		0.001
Part. Cd	0.002	0.001	0.001	0.001	0.002	0.001	0.001		
Diss. Co	0.04	0.03	0.03	0.03	0.03	0.04	0.03	0.04	0.1
Part. Co	0.005	0.003	0.009	0.007	0.014	0.019	0.022	0.02	
Diss. Cu	2.7	2.0	1.4	1.4	1.38	1.43	1.44	0.50	1.4
Part. Cu	0.14	0.11	0.17	0.08	0.20	0.24	0.11	0.06	
Diss. Fe	10.6	27.0	79.4	78.5	84.8	99.4	86.9	492	50.0
Part. Fe	12.6	25.2	44.4	47.0	58.4	71.0	65.5	340	
Diss. Mn	7.4	8.7	4.4	4.6	4.8	7.9	4.7	10.2	10.0
Part. Mn	23.6	12.2	6.9	5.1	6.4	6.0	6.4	6.0	
Diss. Mo	0.69	0.33	0.19	0.19	0.18	0.18	0.18	0.30	0.8
Part. Mo	0.006	0.002	0.002	0.002	0.003	0.004	0.004	0.07	
Diss. Ni	1.71	1.43	1.13	1.10	1.14	1.20	1.17	0.35	0.4
Part. Ni	0.21	0.14	0.15	0.12	0.15	0.17	0.15	0.03	
Diss. Pb	0.02	0.03	0.03	0.04	0.04	0.04	0.11	0.04	0.04
Part. Pb	0.02	0.01	0.02	0.01	0.02	0.04	0.03	0.06	
Diss. Zn	0.29	0.39	0.62	0.44	0.53	0.72	0.98	0.74	0.2
Part. Zn	0.3	0.2	0.4	0.3	0.4	1.1	0.7		

[a] Averages of five samples for each station along the Kola River for the period July 2001–July 2002.
[b] Filtered samples, < 0.22 μm.
[c] Filtered samples, particles > 0.22 μm.
[d] Average of 90 samples from the Kalix River for the period 1990–1992 (Ingri 1996).
[e] Average river water (Meybeck *et al.* 1992).

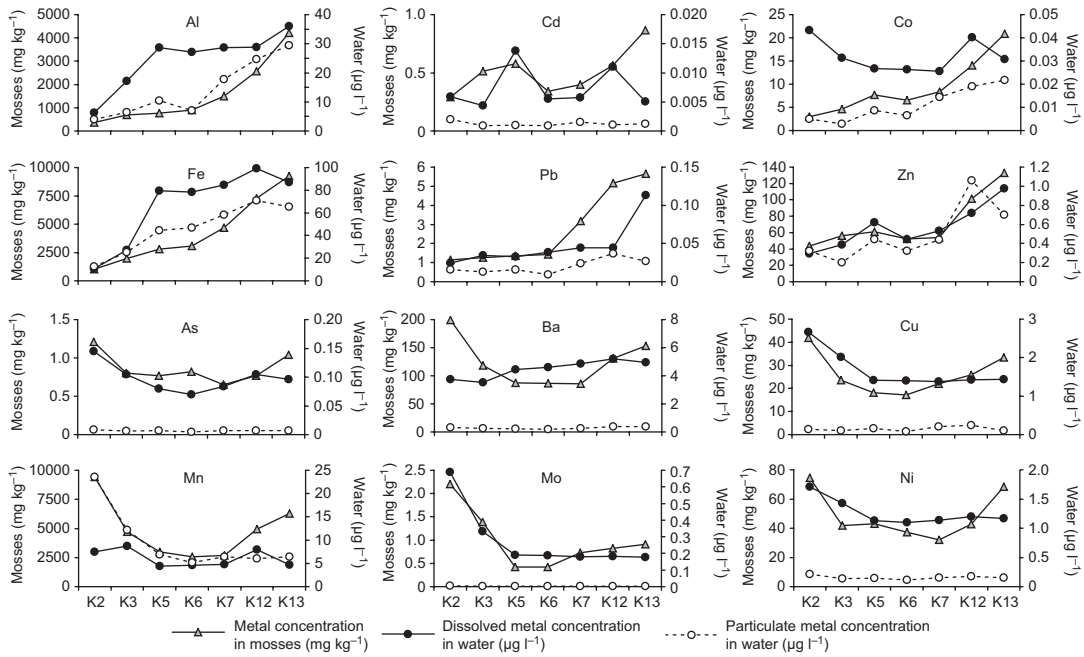


Fig. 3. Distributions of average dissolved (< 0.22 µm) and particulate (> 0.22 µm) metal concentrations in the Kola River (right *y*-axis; $n = 5$ for each sampling site, July 2001–July 2002). Corresponding average metal concentrations in whole shoots of the aquatic bryophytes *Fontinalis* spp. (K2–K7) and *Hygrohypnum ochraceum* (K12–K13) (left *y* -axis; $n = 5$–10 for each sampling site, July 2001 and July 2002).

U-test: $p < 0.05$). The ratios were highest at site K13 for all the metals investigated except for As, Ba, Pb and Zn (Table 2) and reached values of up to ($\times 10^3$): Mn (569), Co (399), Cd (138), Al (64), Fe (61), Ni (52), Cu (22), and Mo (5). The highest enrichment ratios for Zn (95), Pb (64), Ba (49) and As (11) were recorded at sites K3, K12, K2 and K6, respectively.

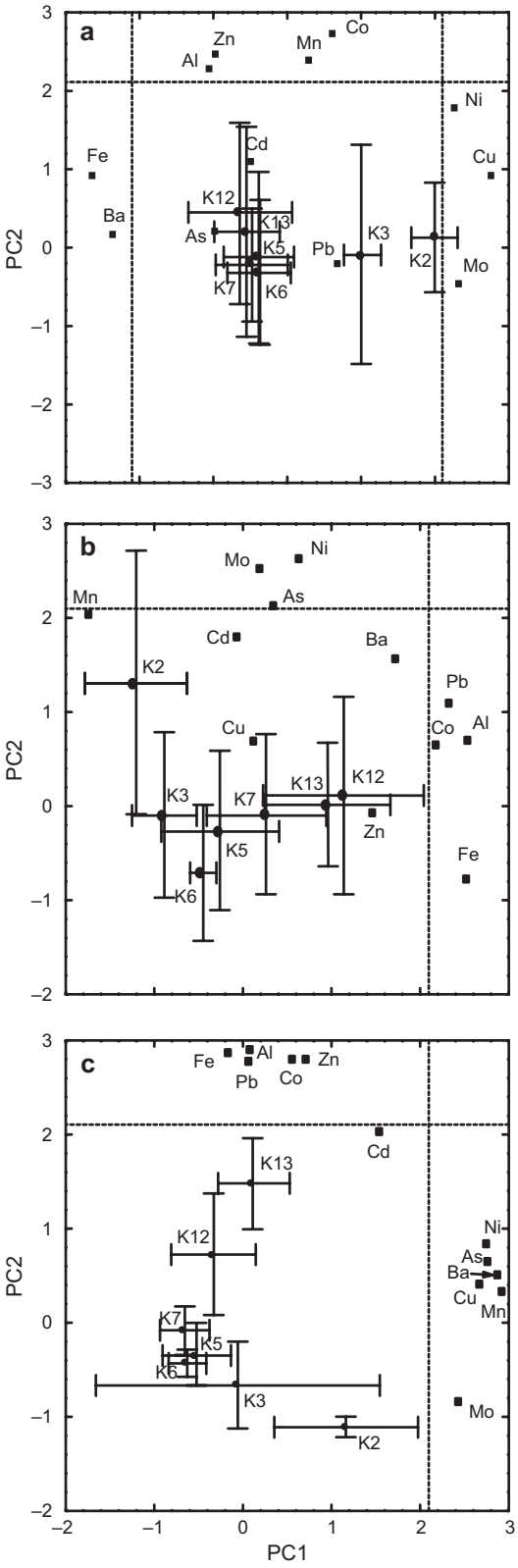
Comparison with the reference rivers

Concentrations of As, Ba, Cd, Co, Fe, Mn, Mo and Pb in the water at the mouth of the Kola River (K13) were close to or even below those in the relatively pristine, much larger Kalix River, whereas those of dissolved Al, Cu and Ni exceeded those in the Kalix River by a factor of three. The comparison with "average river water" (Meybeck *et al*. 1992) showed that Fe, Pb, Cd, Zn and Ni were elevated, while the levels of the other elements were below average (Table 1).

Comparison with the reference rivers (both in northern Finland, Norway and Sweden) showed elevated concentrations of Cu and Ni in the aquatic bryophytes of the Kola River (Mann-Whitney *U*-test: $p < 0.05$) (Fig. 5). Most other metal concentrations in the bryophytes from the Kola River were similar to or lower than those in the relatively pollutant-free reference

Table 2. Enrichment ratios (amount of metal in whole shoots of aquatic bryophytes divided by total (dissolved + particulate) concentrations of that metal in water) ($\times 10^3$). Highest enrichment ratios in boldface.

Element	K2	K3	K5	K6	K7	K12	K13
Al	35	29	19	27	32	48	**64**
AS	8	7	9	**11**	7	7	10
Ba	**49**	31	19	18	17	23	29
Cd	37	98	39	52	55	47	**138**
Co	63	136	218	199	209	236	**399**
Cu	15	11	12	12	14	16	**22**
Fe	45	38	23	25	33	43	**61**
Mn	303	226	264	261	241	354	**569**
Mo	3	4	2	2	4	4	**5**
Ni	39	27	34	30	25	31	**52**
Pb	29	27	28	30	46	**64**	40
Zn	71	**95**	57	68	55	57	79



rivers. Cobalt concentrations in the Kola River were significantly lower ($p < 0.05$) than in the Näätämöjoki and As, Fe and Pb concentrations significantly lower than in the rivers in northern Sweden. On the other hand, in addition to Cu and Ni, the aquatic bryophytes (whole shoots) from the headwaters of the Kola River (K2), close to the mining areas, showed concentrations of Ba and Mo that were twice as high as in the Näätämöjoki. Likewise, Al, Cu and Ni were higher in the mosses from the estuary of the Kola River (K13) than in the Näätämöjoki. Comparing our results with the data from the Tenojoki (Hämäläinen *et al*. 1996), the terminal tips and whole shoots of the Kola River mosses generally had elevated concentrations of Al, Cu and Ni ($p < 0.05$). No definite conclusions could be drawn, however, with regard to Cd and Zn concentrations in the bryophytes from the Kola River, which were elevated as compared with those in the Tenojoki bryophytes ($p < 0.05$) but lower than those in the Näätämöjoki bryophytes ($p < 0.05$).

Discussion

The element concentrations in terrestrial mosses on the Kola Peninsula are related to dust emissions from the open-cast mining, crushing, stockpiling, transport and handling of ore from localised (open cut pits) and extensive (road base materials) sources in the mining district. This geogenic dust is reported to display positive anomalies of Al and Ba, for instance, in terrestrial mosses around Monchegorsk and Olenegorsk (de Caritat *et al*. 2001). Metals of anthropogenic origin, such as Cu and Ni, are also deposited in

Fig. 4. Mean scores at each sampling site (± SD) on the first and second principal components extracted from the 12 metal variables for (**a**) the dissolved fraction (explaining 60.1% of the variance, (**b**) the suspended fraction (explaining 57.9% of the variance), and (**c**) metal concentrations in whole moss shoots (explaining 87.9% of the variance). The factor loadings ($\times 3$, $| > 2.1$, indicated with dashed lines) were used for the interpretation of the PCs. Thus, PC1 of **a**, for example, represents mainly a gradient of increased concentrations of Cu, Mo and Ni. The axes were subjected to varimax normalized rotation.

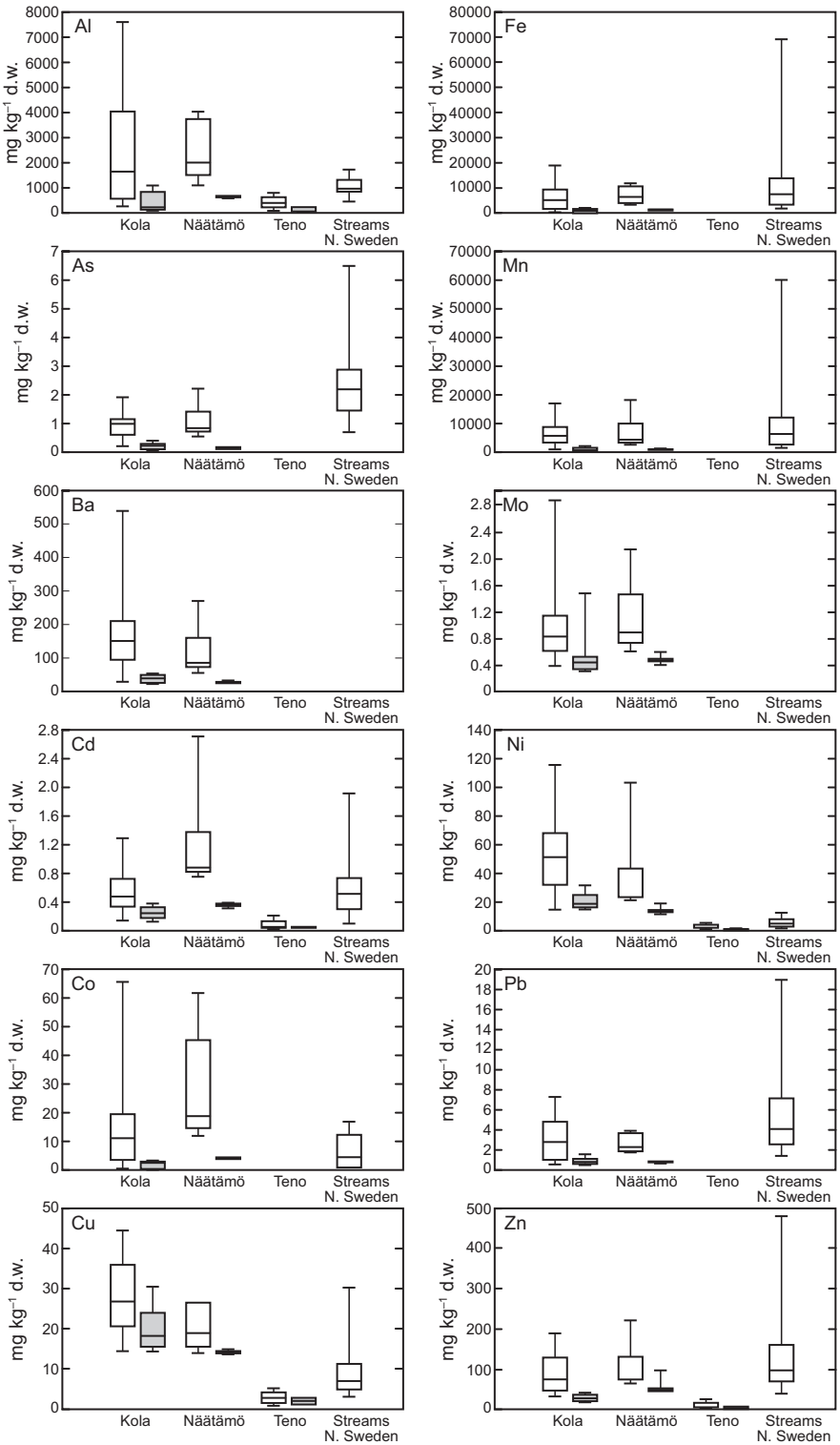


Fig. 5. Median metal concentrations in whole (open boxes) and terminal shoots (filled boxes) of bryophytes in the Kola River and the references sites: the Näätämöjoki, Tenojoki and streams draining woodlands in northern Sweden. Boxes represent 25% percentiles and whiskers 5% percentiles.

the river basins of the Kola Peninsula on a year-round basis, from where they are transported into the water bodies with the melting snow and can also be washed out of the topsoil layer. Clear regional variations can be found in polluted and pristine stream waters on the Kola Peninsula and neighbouring areas. Local, short-time fluctuations in element concentrations can mainly be explained in terms of the lithology of the catchments and the nature of the local anthropogenic emission sources. The most polluted areas within the Kola Peninsula are restricted in spatial extent, but the contaminants are constantly and effectively transported from their original areas of deposition to the rivers and lakes (de Caritat *et al*. 1996a, 1996b). The present results of elevated Cu and Ni concentrations in the aquatic bryophytes of the Kola River correspond well to the hydrochemical results obtained here and reflect the impact of about 70 years of extensive Cu and Ni mining and smelting in the region (Reimann *et al*. 1998, Dauvalter *et al*. 2000).

The metal concentrations in mosses showed clear patterns along the Kola River (Fig. 3), and the metals could be classified into two groups, with Al, Cd, Co, Fe, Pb and Zn forming group 1, which exhibits an almost constant increase from the headwaters (K2) to the river mouth (K13) (Figs. 3 and 4c), and As, Ba, Cu, Mn, Mo and Ni forming group 2, which shows its highest concentrations in the headwaters (K2), relatively low concentrations in the middle parts of the river (K5, K6 and K7) and enhanced concentrations at the mouth (K12 and K13) (Figs. 3 and 4c).

The moss pattern for each metal in these two groups reflects the particulate metal concentrations or the dissolved metal fraction, respectively. For Al, Fe and Co, the moss pattern closely resembles the particulate fractions of these elements in the water (Fig. 3), in spite of the fact that the dissolved concentrations were much higher than the particulate fractions, especially in the middle part of the river (K5, K6 and K7). For the remaining elements in group 1, Cd, Pb and Zn, the correlations with the dissolved or particulate fractions were less clear. In group 2, the moss patterns for As, Cu, Mo, and Ni reflect the dissolved fraction, whereas the Ba and Mn patterns reflect the particulate fraction (Fig. 3).

A close correlation between particulate Mn and the mosses is seen upstream of stations K12 and K13 (Fig. 3), while at K12, and especially at K13, there is a large relative enrichment of Mn in the mosses as compared with the total metal concentrations, as also seen for Al, Cd, Co, Cu, Fe, Mo and Ni (Table 2). The increase in metal concentrations in mosses in the lower part of the Kola River basin is the product of a diverse range of factors. The location of site K13 in the city of Kola, close to a road with heavy traffic and a railway line, together with other possible domestic and industrial sources of pollutants, has most likely increased metal contamination in the estuary. As described by various authors (e.g. Bengtsson and Lithner 1981, Mouvet *et al*. 1993, Philips and Rainbow 1993, Claveri *et al*. 1995, Cenci 2000), mosses represent real integrators of elements in water, as the high accumulation velocity achieved in their tissues records every variation, even between water sampling periods. The elevated levels at K13 may reveal past or present exposure of the mosses to unknown sources of local contamination. Occasional influences from the creeks Medveziy and Zemlanoy, which are polluted by agricultural sources and enter the Kola River about 200 metres upstream of site K12, cannot be excluded. These creeks have highly elevated values for EC (400–530 μS cm^{-1}), alkalinity (150–170 mg l^{-1}), NH_4-N (18 and 8 mg l^{-1} respectively), NO_2-N + NO_3-N (127 and 19 mg l^{-1} respectively), phosphorus (dissolved + particulate) (1900 and 700 μg l^{-1}, respectively) and DOC (35 and 15 mg l^{-1}, respectively) (Pekka *et al*. 2004), and their concentrations of dissolved Co, Mn, Fe and Zn, and particulate Ba, Fe, Mo, Pb and Zn are up to 60 and 170 times higher, respectively, than in the river (Pekka *et al*. 2004). Relatively enhanced concentrations of these elements in the dissolved and particulate phases, respectively, were also observed at K12 (Figs. 2a–c, 3 and 4a–b).

Furthermore, the possible higher enrichment ratios of the bryophyte species *Hygrohypnum ochraceum* (sampled at sites K12 and K13) relative to *Fontinalis* spp. (K2–K7) may to some extent contribute to the increased metal accumulation at these sites. Species-specific differences in the morphology of moss leaflets, which take up nutrients as well as pollutants, cell wall com-

position and the ratio of stem and branch tissue to leaf tissue can substantially affect the metal accumulation capacity of aquatic bryophytes (Glime 1992, Bleuel *et al*. 2005). Although our moss data, when examined together with the water samples, did not give us any reason to suspect major differences in metal accumulation capacity between *F. dalecarlica* (site K6) and *F. antipyretica* (sites K2, K3, K5 and K7), comparisons of the results for the Kola River with data for the reference rivers should be approached with caution in view of the possibility of divergences in metal accumulation capacity between bryophyte species. Although abilities and sensitivities differ, all the bryophyte taxa are good accumulators of heavy metals (Glime 1992). Many pollution surveys with aquatic bryophytes include more than one species, as single species does not always grow, or is not abundant enough for sampling, throughout the survey area (Say *et al*. 1981, Samecka-Cymerman and Kempers 1998, Vanderpoorten 1999, Nimis *et al*. 2002, Samecka-Cymerman *et al*. 2002).

The increased concentrations of Fe and Al in the river between K2–K3 and K5–K7 can most likely be explained by the inflow of these metals in the form of dissolved organic complexes and/or colloidal oxyhydroxides ($< 0.22\ \mu$m) mixed with organic matter from the vast peatlands in the middle parts of the Kola River basin. High dissolved concentrations of these elements and of DOC have been measured in the Kitsa River, for example (Fig. 1, Pekka *et al*. 2004). This increase in dissolved Al and Fe was not observed in the mosses, however.

Metal concentrations in mosses discriminate more clearly among sampling sites than do metal concentrations in the dissolved and particulate fractions in river water. In addition, discrimination using the moss PCA model was based on almost the entire spectrum of elements (11 out of the 12 measured), whereas only nine and seven of these elements, respectively, were significant for discrimination among the sampling sites in the case of the dissolved and particulate PCA models. Thus metal concentrations in whole moss shoots appear to be a more sensitive tool than metal concentrations in water for discriminating among sampling sites along the Kola River. It should be borne in mind that metal concentrations in bryophytes reflect accumulated concentrations (Bengtsson and Lithner 1981).

The geological characteristics of the catchment area, hydrochemical parameters in the flow direction and anthropogenic inputs all influence the concentrations of heavy metals in water and their accumulation in aquatic bryophytes (Siebert *et al*. 1996). Correlations between element concentrations in water and in mosses have been demonstrated previously (e.g. Goncalves *et al*. 1994, Samecka-Cymerman and Kempers 1998). In addition to the concentrations in the water, the enrichment ratios of the bryophyte species, flow velocity, temperature, light and oxygen conditions, pH, sulphate concentration, nitrite, ammonia, filterable reactive phosphate and complexation by dissolved organic carbon (DOC) appear to be the important physical and chemical variables determining the accumulation of metals in aquatic bryophytes (Bengtsson and Lithner 1981, Lopez and Carballeira 1993, Siebert *et al*. 1996, Gstoettner and Fisher 1997).

Our results suggest that both evaluation methods, i.e. measuring heavy metal concentrations in water and in bryophytes, reflect the degree of pollution in the Kola River. Significant correlations between metals in the moss and water samples were found for the dissolved and particulate phases in water. Several authors have maintained that isolated water analyses are not meaningful enough to detect overall pollution situations over a given period, and that peak values for short-term pollution at individual sites cannot always be detected by water analyses (e.g. Bruns *et al*. 1997). Our analyses strongly suggest that, in order to gain a comprehensive understanding of the pollution status of rivers, measurements of bryophyte metal concentrations should be included in the sampling, especially when flowing waters are to be sampled on only one or a few occasions. Based on the finding of a fairly tolerable metal contamination situation in the Kola River, further monitoring of the degree of pollution there is not necessarily needed in the form of constant analyses of heavy metals in the water, but moss sampling should be carried out at regular intervals over longer periods. This is justified since metals accumulated in mosses pose a risk for food chain effects including accumulation of metals in fish feeding on moss-

dwelling invertebrates (Dallinger and Kautzky 1985). Accurate sources and reasons for differences in specific metals between sampling sites and for possible differences in metal accumulation rate between moss species should be sought in the future.

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